

AF
-- A heat-sensitive recording material was obtained in the same manner as in Example 7 except that 10 parts of a fluoran-based leuco dye capable of forming black color, i.e., 3-di(n-butyl)amino-6-methyl-7-anilinofluoran (melting point: 182°C) was used instead of 10 parts of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation of Dispersion B in Example 7. --

REMARKS

The specification has been amended to correct clerical errors. The amendments to the paragraphs on pages 2, 3, 11 and 12 to correct the spelling of --toluidino-- are supported, inter alia, in Table 2 on page 41 of the specification. (See the meanings of "LDK" and "LDKM").

The amendment to the paragraph on page 29 is clear on its face.

The amendment to Comparative Example 4 on page 34 to correct the name of the leuco dye is supported by the description of Table 1 on page 40 and Comparative Examples 1-3 and 5-7 on pages 33-35.

Attached hereto is a marked-up version of the changes made to

APPLICATION SN: 09/988,466
PRELIMINARY AMENDMENT

PATENT

the specification by the current amendment. The attachment is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE."

In the event any additional fees are required, please charge our Deposit Account No. 111833.

Respectfully submitted,

KUBOVCIK & KUBOVCIK


Keiko Tanaka Kubovcik
Reg. No. 40,428

Atty. Case No. SAE-026
The Farragut Building
Suite 710
900 17th Street, N.W.
Washington, D.C. 20006
Tel: (202) 887-9023
Fax: (202) 887-9093
KTK/cfm

VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE SPECIFICATION:

The paragraph beginning at page 2, line 13 has been amended as follows:

--Unexamined Japanese Patent Publication No. 1996-216528 discloses a heat-sensitive recording material which makes use of 3-(N-ethyl-p-[~~toluidine~~]toluidino)-6-methyl-7-anilinofluoran as a leuco dye, and 4,4'-dihydroxydiphenyl-sulfone or 2,4'-dihydroxydiphenylsulfone as a developer, and states that this recording material has excellent recording sensitivity and undergoes less degree of background fogging in a high temperature environment at 100°C, and has an excellent storage stability of the recorded image (with less decrease in recording density with a lapse of time).--

The paragraph beginning at page 2, line 24 has been amended as follows:

--Unexamined Japanese Patent Publication No. 1997-11620 discloses a heat-sensitive recording material which makes use of 3-(N-ethyl-p-[~~toluidine~~]toluidino)-6-methyl-7-anilinofluoran

as a leuco dye and 4-hydroxy-4'-isopropoxydiphenylsulfone as a developer, and states that the recording material has excellent recording sensitivity, entails less decrease in the recording density of the recorded image in a high temperature environment of 80°C, undergoes less degree of background fogging, and has excellent resistance of the recorded image to humidity and water.--

The paragraph beginning at page 3, line 10 has been amended as follows:

--Further, Unexamined Japanese Patent Publication No.1999-291633 discloses a heat-sensitive recording material that makes use of 3-(N-ethyl-p-[~~toluidine~~]toluidino)-6-methyl-7-anilinofluoran or 3-(N-ethyl-p-[~~toluidine~~]toluidino)-6-methyl-7-(p-[~~toluidine~~]toluidino)fluoran as a leuco dye and bis(3-allyl-4-hydroxyphenyl)sulfone as a developer, and states that the recording material is excellent in recording sensitivity, heat resistance (in a high temperature environment of 80°C), humidity resistance, plasticizer resistance, water resistance and light resistance.--

The paragraph beginning at page 11, line 16 has been amended as follows:

--Examples of the specific leuco dye include fluoran-based leuco dyes which form black color, such as 3-pyrrolidino-6-methyl-7-anilinofluoran (melting point: 225°C), 3-piperidino-6-methyl-7-anilinofluoran (melting point: 226°C), 3-diethylamino-6-methyl-7-anilinofluoran (melting point: 192°C), 3-(N-ethyl-p-[toluidine]toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C), 3-(N-ethyl-p-[toluidine]toluidino)-6-methyl-7-(p-[toluidine]toluidino)fluoran (melting point: 227°C), 3-diethylamino-7-(o-chloroanilino)fluoran (melting point: 218°C), 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-anilinofluoran (melting point: 202°C), fluoran-based leuco dyes which form red color, such as 3-diethylamino-benzo[α]fluoran (melting point: 219°C), 3-diethylamino-7,8-benzofluoran (melting point: 217°C), and the like. Two or more of these specific leuco dyes can also be used in admixture.--

The paragraph beginning at page 12, line 7 has been amended as

follows:

--Among these, fluoran-based leuco dyes which form black color, and especially 3-(N-ethyl-p-[~~toluidine~~] toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) is preferable because the resulting heat-sensitive recording material is excellent in background fogging resistance, dynamic recording sensitivity and light resistance of the recorded image.--

The paragraph beginning at page 28, line 17 has been amended as follows:

--A composition composed of 40 parts of calcined clay (trade name: Ansilex, oil absorption 110 ml/100 g, made by Engelhard Corporation), 100 parts of a 40% dispersion of organic hollow particles having an average particle diameter of 1.0 μm (inside diameter/outside diameter: 0.7, shell material: polystyrene), 1 part of a 40% aqueous solution of sodium salt of polyacrylic acid, 14 parts of a styrene-butadiene latex with a solids concentration of 48%, 50 parts of a 10% aqueous solution of polyvinyl alcohol (degree of saponification: 88%, degree of polymerization: 1000), and 40

parts of water was mixed and stirred to obtain an undercoat layer coating composition.--

The paragraph beginning at page 34, line 18 has been amended as follows:

--A heat-sensitive recording material was obtained in the same manner as in Example 7 except that 10 parts of a fluoran-based leuco dye capable of forming black color, i.e., 3-di(n-butyl)amino-6-methyl-7-anilinofluoran (melting point: 182°C) was used instead of 10 parts of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation of Dispersion B in Example 7.--

HEAT-SENSITIVE RECORDING MATERIAL

BACKGROUND OF THE INVENTION

5 (1) Field of the Invention

The present invention relates to a heat-sensitive recording material that utilizes a color forming reaction between a leuco dye and a developer.

10 (2) Description of the Related Art

Heat-sensitive recording materials which utilize a color forming reaction between a leuco dye and a developer are relatively inexpensive and the required recording device is compact and easy to maintain, and therefore 15 these materials are used in a wide range of fields, such as recording media for facsimile machines, word processors, various types of computers, and other such applications.

As the field of use of these heat-sensitive recording materials has expanded, the environments in 20 which they are used have become increasingly severe. There is a need for a material that will simultaneously satisfy such requirements as good resistance of the non-recorded image portion to heat and light, good storage stability of the recorded image, and high-speed recording. 25 So far, however, if the heat resistance and light

resistance of the non-recorded image portion are improved, there has generally been a decrease in the storage stability of the recorded image and in recording sensitivity.

5 International Publication WO00/35679 discloses that a heat-sensitive recording material which makes use of N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea as a developer is superior in terms of recording sensitivity, resistance of the recorded image to oil, 10 water, plasticizers and so forth, and resistance to background fogging, and other properties, but no specific measurement data is given.

Unexamined Japanese Patent Publication No. 1996-216528 discloses a heat-sensitive recording material which 15 makes use of 3-(N-ethyl-p-toludino)-6-methyl-7-anilinofluoran as a leuco dye, and 4,4'-dihydroxydiphenylsulfone or 2,4'-dihydroxydiphenylsulfone as a developer, and states that this recording material has excellent recording sensitivity and undergoes less degree of 20 background fogging in a high temperature environment at 100 °C, and has an excellent storage stability of the recorded image (with less decrease in recording density with a lapse of time).

Unexamined Japanese Patent Publication No. 1997-25 11620 discloses a heat-sensitive recording material which

makes use of 3-(N-ethyl-p-toludino)-6-methyl-7-anilinofluoran as a leuco dye and 4-hydroxy-4'-isopropoxydiphenylsulfone as a developer, and states that the recording material has excellent recording sensitivity,
5 entails less decrease in the recording density of the recorded image in a high temperature environment of 80 °C, undergoes less degree of background fogging, and has excellent resistance of the recorded image to humidity and water.

10 Further, Unexamined Japanese Patent Publication No.1999-291633 discloses a heat-sensitive recording material that makes use of 3-(N-ethyl-p-toludino)-6-methyl-7-anilinofluoran or 3-(N-ethyl-p-toludino)-6-methyl-7-(p-toludino)fluoran as a leuco dye and bis(3-allyl-4-hydroxyphenyl)sulfone as a developer, and states that the recording material is excellent in recording sensitivity, heat resistance (in a high temperature environment of 80°C), humidity resistance, plasticizer resistance, water resistance and light resistance.
15

20 While these known heat-sensitive recording materials have the respective properties listed above, there is still a need for a heat-sensitive recording material with even better properties, and particularly a heat-sensitive recording material that is excellent in recording sensitivity, heat resistance in an environment of 90 to
25

100°C, light resistance, water resistance, plasticizer resistance, and so forth.

An object of the present invention is to provide a heat-sensitive recording material which has excellent properties such as recording sensitivity, heat resistance, 5 light resistance, water resistance, plasticizer resistance and the like.

BRIEF SUMMARY OF THE INVENTION

10

In a heat-sensitive recording material comprising a support and as formed thereon a heat-sensitive recording layer containing a leuco dye and a developer, the present invention uses, as one means for achieving the above 15 object, N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)-phenylurea as the developer and the heat-sensitive recording layer contains at least one fluoran-based leuco dye having a melting point of 190 to 230°C and/or at least one pigment selected from the group consisting of aluminum 20 hydroxide, amorphous silica, kaolin and talc.

Specifically, the present invention provides the following heat-sensitive recording materials.

1. A heat-sensitive recording material comprising a support and a heat-sensitive recording layer formed on the 25 support and containing a leuco dye and a developer,

the developer being N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea, and
the heat-sensitive recording layer containing (a) at least one fluoran-based leuco dye having a melting point of 190 to 230°C and/or (b) at least one pigment selected from the group consisting of aluminum hydroxide, amorphous silica, kaolin and talc.

2. The heat-sensitive recording material according to Item 1, wherein the heat-sensitive recording layer contains N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea as the developer and (a) at least one fluoran-based leuco dye with a melting point of 190 to 230°C and (b) at least one pigment selected from the group consisting of aluminum hydroxide, amorphous silica, kaolin and talc.

3. The heat-sensitive recording material according to Item 2, wherein the fluoran-based leuco dye with a melting point of 190 to 230°C is 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran.

4. The heat-sensitive recording material according to Item 2, wherein the fluoran-based leuco dye with a melting point of 190 to 230°C is 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran and the pigment is aluminum hydroxide.

5. The heat-sensitive recording material

according to Item 2, wherein the heat-sensitive recording layer further contains a sensitizer.

6. The heat-sensitive recording material according to Item 5, wherein the sensitizer is at least 5 one member selected from the group consisting of 2-naphthyl benzyl ether, 1,2-di(3-methylphenoxy)ethane and 1,2-diphenoxoethane.

7. The heat-sensitive recording material according to Item 1, wherein the heat-sensitive recording 10 layer contains N-p-toluenesulfonyl-N'-3-(p-toluene-sulfonyloxy)phenylurea as the developer and (b) at least one pigment selected from the group consisting of aluminum hydroxide, amorphous silica, kaolin and talc.

8. The heat-sensitive recording material 15 according to Item 7, wherein the heat-sensitive recording layer contains a fluoran-based leuco dye with a melting point under 190°C.

9. The heat-sensitive recording material according to Item 7, wherein the pigment is aluminum 20 hydroxide.

10. The heat-sensitive recording material according to Item 7, wherein the heat-sensitive recording layer further contains a sensitizer.

11. The heat-sensitive recording material 25 according to Item 10, wherein the sensitizer is at least

one member selected from the group consisting of 2-naphthyl benzyl ether, 1,2-di(3-methylphenoxy)ethane and 1,2-diphenoxylethane.

12. The heat-sensitive recording material
5 according to Item 1, wherein the heat-sensitive recording layer contains N-p-toluenesulfonyl-N'-3-(p-toluene-sulfonyloxy)phenylurea as the developer and (a) at least one fluoran-based leuco dye with a melting point of 190 to 230°C.

10 13. The heat-sensitive recording material according to Item 12, wherein the fluoran-based leuco dye with a melting point of 190 to 230°C is 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran.

14. The heat-sensitive recording material
15 according to Item 12, wherein the heat-sensitive recording layer further contains a sensitizer.

16. The heat-sensitive recording material
according to Item 14, wherein the sensitizer is at least one member selected from the group consisting of 2-naphthyl benzyl ether, 1,2-di(3-methylphenoxy)ethane and 1,2-diphenoxylethane.

25 17. The heat-sensitive recording material according to Item 1, which further comprises, between the support and the heat-sensitive recording layer, an undercoat layer comprising as the main components a binder

and at least one member selected from the group consisting of (i) an oil-absorbing pigment with an oil absorption (according to JIS K 5101) of at least 70 ml/100 g and (ii) organic hollow particles.

5 17. The heat-sensitive recording material according to Item 1, which further comprises, on the heat-sensitive recording layer, a protective layer comprising as the main components a binder which has a film-forming ability and, if desired, a pigment.

10 18. The heat-sensitive recording material according to Item 16, which further comprises, on the heat-sensitive recording layer, a protective layer comprising as the main components a binder which has a film-forming ability and, if desired, a pigment.

15

DETAILED DESCRIPTION OF THE INVENTION

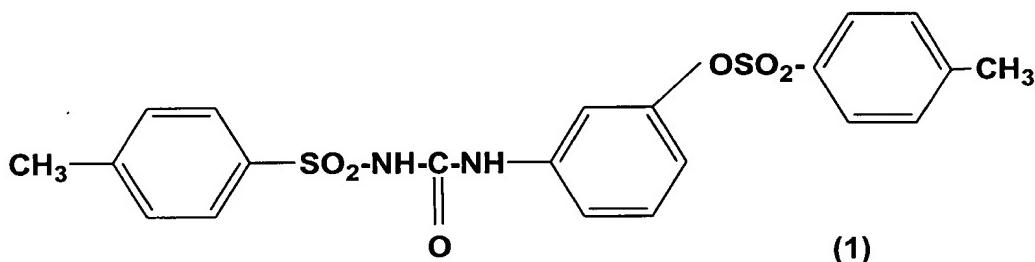
As stated above, the present invention is characterized by the use of a specific developer, namely,
20 N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea, and a specific leuco dye, namely, at least one fluoran-based leuco dye with a melting point of 190 to 230°C, and/or a specific pigment, namely, at least one member selected from the group consisting of aluminum hydroxide,
25 amorphous silica (including one obtained from colloidal

silica), kaolin and talc.

It is particularly favorable in the present invention that the above-mentioned specific developer is used in combination with the above-mentioned specific leuco dye 5 and the above-mentioned specific pigment.

Developer

The specific developer, namely, N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)-phenylurea, to be used in the present invention is a compound represented by the 10 following formula (1).



This compound is known and is commercially available.

While there is no particular restriction on the amount of the above-mentioned specific developer to be 15 used, the specific developer is preferably used in an amount of about 10 to 60 wt%, more preferably about 20 to 40 wt%, based on the heat-sensitive recording layer.

Pigment

The pigment used in the present invention is at 20 least one of the specific pigments selected from the group

consisting of aluminum hydroxide, amorphous silica (including one obtained from colloidal silica), kaolin and talc.

There is no particular restriction on the amount of
5 the specific pigment to be used, but the specific pigment is preferably used in an amount of about 3 to 50 wt%, more preferably about 5 to 25 wt%, based on the heat-sensitive recording layer. The use of this specific pigment results in excellent properties such as recording sensitivity,
10 heat resistance, light resistance, water resistance and plasticizer resistance, and additionally produces the effect of improving resistance to background fogging caused by hot water (hereinafter referred to as "hot water background fogging resistance"). The heat-sensitive
15 recording materials having excellent hot water background fogging resistance is advantageously used for lottery tickets, horse race tickets and the like, because the recorded images formed thereon are legible even if they are contacted with hot water, hot coffee, hot tea, etc.

20 Of the pigments listed above, the use of aluminum hydroxide is particularly favorable because the color density of the recorded image during heat-sensitive recording is higher.

The average particle diameter of the primary
25 particles of the specific pigment can be selected from a

wide range, but is preferably in the range of about 0.01 to 5 μm .

Leuco dye

The specific leuco dye to be used in the present 5 invention is a fluoran-based leuco dye with a melting point of 190 to 230°C.

When a fluoran-based leuco dye having a melting point of lower than 190°C is used, severe background fogging may occasionally occur when the heat-sensitive 10 recording material is exposed to a high temperature of 90 to 100°C. When a fluoran-based leuco dye having a melting point of higher than 230°C is used, the recording sensitivity might be pronouncedly reduced. In general, it is particularly preferable that the specific leuco dye has 15 a melting point of 200 to 220°C.

Examples of the specific leuco dye include fluoran-based leuco dyes which form black color, such as 3-pyrrolidino-6-methyl-7-anilinofluoran (melting point: 225°C), 3-piperidino-6-methyl-7-anilinofluoran (melting 20 point: 226°C), 3-diethylamino-6-methyl-7-anilinofluoran (melting point: 192°C), 3-(N-ethyl-p-toludino)-6-methyl-7-anilinofluoran (melting point: 206°C), 3-(N-ethyl-p-toludino)-6-methyl-7-(p-toludino)fluoran (melting point: 227°C), 3-diethylamino-7-(o-chloroanilino)fluoran (melting 25 point: 218°C), 3-(N-cyclohexyl-N-methylamino)-6-methyl-7-

anilinofluoran (melting point: 202°C), fluoran-based leuco dyes which form red color, such as 3-diethylamino-benzo[α]fluoran (melting point: 219°C), 3-diethylamino-7,8-benzofluoran (melting point: 217°C), and the like.

- 5 Two or more of these specific leuco dyes can also be used in admixture.

Among these, fluoran-based leuco dyes which form black color, and especially 3-(N-ethyl-p-toludino)-6-methyl-7-anilinofluoran (melting point: 206°C) is 10 preferable because the resulting heat-sensitive recording material is excellent in background fogging resistance, dynamic recording sensitivity and light resistance of the recorded image.

The above-mentioned specific leuco dye is preferably 15 used in an amount of about 5 to 35 wt%, more preferably about 10 to 25 wt%, based on the heat-sensitive recording layer.

Sensitizer

If desired, the heat-sensitive recording layer may 20 contain one or more various known sensitizers in order to further enhance the recording sensitivity. Specific examples of such sensitizers include parabenzylbiphenyl, dibenzyl terephthalate, phenyl 1-hydroxy-2-naphthoate, dibenzyl oxalate, di(o-chlorobenzyl) adipate, 2-naphthyl 25 benzyl ether, 1,2-diphenoxymethane, 1,2-di(3-

methylphenoxy)ethane, 1,2-di(3,4-dimethylphenyl)ethane,
1,3-bis(2-naphthoxy)propane, di(p-methylbenzyl) oxalate,
di(p-chlorobenzyl) oxalate, meta-terphenyl, diphenyl,
benzophenone, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole
5 and the like.

Among these, 2-naphthyl benzyl ether, 1,2-di(3-methylphenoxy)ethane and 1,2-diphenoxymethane are particularly favorable because they are effective for achieving excellent dynamic recording sensitivity and
10 outstanding heat resistance of the unrecorded portion.

The amount of the sensitizer to be used in the heat-sensitive recording layer is about 1 to 10 weight parts, preferably about 1 to 5 weight parts, per weight part of the specific leuco dye.

15 Optional components

At least the specific developer, (a) the specific leuco dye and/or (b) the specific pigment are used in the heat-sensitive recording layer of the present invention, and if desired, other leuco dyes, other developers, and
20 other pigments can also be used, and other components can also be added, insofar as they do not impair the desired effects of the present invention.

If such optional components are used, for example, in a heat-sensitive recording layer containing the
25 specific developer, the specific leuco dye and the

specific pigment, said other developer can be used in an amount of not more than 10 wt%, particularly about 1 to 10 wt%, based on the specific developer; said other leuco dye can be used in an amount of not more than 10 wt%,
5 particularly about 1 to 10 wt%, based on the specific leuco dye, and said other pigment can be used in an amount of not more than 10 wt%, particularly about 1 to 10 wt%, based on the specific pigment. It is also preferable that the total amount of the specific pigment and said other
10 pigment is about 5-55 wt%, more preferably about 6-30 wt%, based on the heat-sensitive recording layer.

Examples of said other leuco dyes include
3-diethylamino-7-(m-trifluoromethylanilino)fluoran,
3-(N-isoamyl-N-ethylamino)-7-(o-chloroanilino)fluoran,
15 3-diethylamino-6-chloro-7-anilinofluoran, 3-di(n-butyl)amino-6-methyl-7-anilinofluoran, 3-di(n-pentyl)amino-6-methyl-7-anilinofluoran, 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, and 3-(4-diethylamino-2-methylphenyl)-3-(4-dimethylaminophenyl)-6-
20 dimethylaminophthalide.

Examples of said other developers include
4,4'-isopropylidenediphenol, 4,4'-dihydroxydiphenyl ether,
3,3'-diallyl-4,4'-dihydroxydiphenylsulfone,
4,4'-cyclohexylidenediphenol, 1,1-bis(4-hydroxyphenyl)-
25 ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 4,4'-

dihydroxydiphenyl sulfide, 4,4'-thiobis(3-methyl-6-tert-butylphenol), 4,4'-dihydroxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone, 4-hydroxy-4'-isopropoxydiphenylsulfone, benzyl 4-hydroxybenzoate, zinc 5 3-(α -methylbenzyl) salicylate, zinc 3,5-di-tert-butylsalicylate, and zinc 4-[3-(p-tolylsulfonylphenoxy-ethoxy)cumyl] salicylate.

Examples of said other pigments include precipitated calcium carbonate, ground calcium carbonate, calcined 10 kaolin, titanium oxide, magnesium carbonate, barium sulfate, urea-formalin resin filler and the like.

A print stability-improving agent can also be contained in the heat-sensitive recording layer in order to further enhance the storage stability of the recorded 15 image. Examples of such print stability-improving agent include 1,1,3-tris(2-methyl-4-hydroxy-5-cyclohexylphenyl)-butane, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl)-butane, 1,1-bis(2-methyl-4-hydroxy-5-tert-butylphenyl)-butane, 4,4'-(1,4-phenylenebis(1-methylethylidene))-bisphenol, 4,4'-(1,3-phenylenebis(1-methylethylidene))-bisphenol, 4-benzyloxyphenyl-4'-(2-methyl-2,3-epoxypropyloxy)phenylsulfone, 4-(2-methyl-1,2-epoxyethyl)diphenylsulfone, 1,3,5-tris(2,6-dimethylbenzyl-3-hydroxy-4-tert-butyl)isocyanuric acid and the like. 25 Such print stability-improving agent, if employed, is used

in an amount of about 0.1 to 30 wt%, preferably about 1 to 20 wt%, based on the heat-sensitive recording layer.

Heat-sensitive recording layer

The heat-sensitive recording layer is obtained, for example, as follows. The specific developer, the specific leuco dye and, if desired, a sensitizer and the above-mentioned optional components (such as a print-stability improving agent) are pulverized usually in water serving as a dispersion medium, either jointly or separately, by means of a ball mill, an attritor, a sand mill or like pulverizer to an average particle diameter of about 0.2 to 2.0 μm . Then to the mixture are added a binder, the specific pigment and, if desired, the following one or more auxiliaries, and the resulting mixture is stirred to prepare a heat-sensitive recording layer coating composition. The coating composition is applied to a support and the resulting coating is dried.

The support can be a variety of suitable supports used in this field, and examples thereof include wood-free paper made from non-chlorine bleached pulp, plastic films, base paper containing waste paper, and synthetic paper.

Examples of binders include polyvinyl alcohol, carboxy-modified polyvinyl alcohol, acetoacetyl-modified polyvinyl alcohol, diacetone-modified polyvinyl alcohol, silicon-modified polyvinyl alcohol, oxidized starch,

gelatin, casein, starch-vinyl acetate graft copolymers, styrene-maleic anhydride copolymers, methyl vinyl ether-maleic anhydride copolymers, isopropylene-maleic anhydride copolymers and like water-soluble resins, styrene-
5 butadiene latex, acrylic latex, urethane latex and like water-dispersible resins, etc. The amount of the binder to be used is about 5 to 40 wt%, preferably about 10 to 30 wt%, based on the heat-sensitive recording layer.

Various auxiliaries can be added to the heat-
10 sensitive recording layer coating composition, if so desired. Examples of such auxiliaries include sodium dioctylsulfosuccinate, sodium dodecylbenzenesulfonate, sodium lauryl sulfate, fatty acid metal salts and like surfactants, zinc stearate, calcium stearate, polyethylene
15 wax, carnauba wax, paraffin wax, ester wax and like waxes, glyoxal, urea formalin resin, polyamide resin, polyamideamine-epichlorohydrin resin, adipic acid dihydrazide, boric acid, borax, zirconium ammonium carbonate and like insolubilizers, UV absorbents, anti-
20 foaming agents, fluorescent dyes, coloring dyes, and so forth.

The coating amount of the heat-sensitive recording layer coating composition is about 2 to 12 g/m², preferably about 3 to 7 g/m², on a dry weight basis. The
25 heat-sensitive recording layer coating composition is

applied to the support by a known coating device such as a bar coater, an air knife coater, a blade coater, a gravure coater, a die coater and the like. After the coating layer is dried, the resulting heat-sensitive recording 5 layer can be treated with a super calender, gloss calender or the like to impart smoothness to the surface.

Preferred embodiments

In a preferred embodiment of the present invention, the heat-sensitive recording layer of the heat-sensitive 10 recording material of the present invention contains the above-mentioned specific developer, (a) the above-mentioned specific leuco dye, (b) the specific pigment, and if desired, the above-mentioned sensitizer. In particular, the heat-sensitive recording layer of the 15 heat-sensitive recording material of the present invention preferably contains N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea, (a) 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran, (b) aluminum hydroxide and, if desired, the above-mentioned sensitizer. 20 The heat-sensitive recording material according to this embodiment is advantageous because it is excellent in dynamic recording sensitivity, heat resistance, light resistance, water resistance, hot water background fogging resistance and plasticizer resistance.

Protective layer

If necessary, a protective layer may be provided on the heat-sensitive recording layer in order to enhance the resistance of the recorded image to chemicals and water,
5 or to improve runability during recording. This protective layer is formed by coating the heat-sensitive recording layer with a protective layer coating composition comprising as main components a binder having film-forming ability and, if needed, a pigment, and then
10 drying the resulting coating film.

Examples of the binder to be contained in the protective layer coating composition include completely saponified polyvinyl alcohol, partially saponified polyvinyl alcohol, carboxy-modified polyvinyl alcohol,
15 acetoacetyl-modified polyvinyl alcohol, silicon-modified polyvinyl alcohol, diacetone-modified polyvinyl alcohol, and other such polyvinyl alcohols, starches, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, gelatin, casein, gum arabic, diisobutylene-maleic
20 anhydride copolymer salts, styrene-maleic anhydride copolymer salts, ethylene-acrylic acid copolymer salts, styrene-acrylic acid copolymer salts, styrene-butadiene-based latex, acrylic-based latex, and urethane-based latex.

The foregoing auxiliaries that can be added to the
25 above-mentioned heat-sensitive recording layer coating

composition can also be added to the protective layer coating composition.

Undercoat layer

- 5 If desired, an undercoat layer can also be provided between the support and the heat-sensitive recording layer in order to improve recording sensitivity and runability during recording. The undercoat layer is formed by coating the support with an undercoat layer coating
- 10 composition comprising as main components organic hollow particles and/or an oil-absorbing pigment with an oil absorption (based on JIS K 5101) of at least 70 ml/100 g, and particularly about 80 to 150 ml/100 g, and a binder, and then drying the coating.
- 15 Various oil-absorbing pigments can be used for the above purpose. Typical examples thereof include inorganic pigments such as calcined clay, amorphous silica, precipitated calcium carbonate, talc and the like. Preferably, the average particle diameter of the primary
- 20 particles of this pigment is about 0.01 to 5 μm , particularly about 0.02 to 3 μm . The amount of the oil-absorbing pigment to be used can be selected from a wide range, but it is usually preferable to use the oil-absorbing pigment in an amount of 50 to 95 wt.%,
- 25 particularly about 70 to 90 wt.%, based on the undercoat

layer.

As the organic hollow particles, various known organic hollow particles can be used, and typical examples thereof include particles having a shell made of an 5 acrylic resin, styrene-based resin, vinylidene chloride-based resin or the like and having a void ratio of about 50 to 99%. Herein, the term "void ratio" is defined as (d/D) × 100, wherein d is the inside diameter of the organic hollow particles and D is the outside diameter of 10 the organic hollow particles. It is preferable that the organic hollow particle has an average outside diameter of about 0.5 to 10 μm , particularly about 1 to 5 μm . The amount of the above-mentioned organic hollow particles to be used can be selected from a wide range. Generally, the 15 amount is preferably about 20 to 90 wt.%, particularly about 30 to 70 wt.%, based on the undercoat layer.

The above-mentioned organic hollow particles may be expandable hollow particles. Typical examples of such expandable hollow particles are microcapsules having an 20 average particle diameter of 0.1 to 5 μm , each of which comprises a shell made of, for example, vinylidene chloride resin and butane gas as enclosed in the shell. When the undercoat layer coating composition containing such expandable hollow particles is applied to a support 25 and dried to form an undercoat layer, and the undercoat

layer is then brought into close contact with a plate heated at about 80-150°C, this heat-treatment causes the butane gas enclosed in the microcapsules to expand with the result that the microcapsules expand to an average 5 particle diameter of 1-30 µm.

When the above-mentioned oil-absorbing inorganic pigment is used in combination with the organic hollow particles, the oil-absorbing pigment and the organic hollow particles are used in an amount within the range 10 specified above, and the combined amount of the oil-absorbing inorganic pigment and the organic hollow particles is preferably about 40 to 90 wt.%, particularly about 50 to 80 wt.%, based on the undercoat layer.

It is preferable that the above-mentioned binder is 15 selected from the binders to be used in the heat-sensitive recording layer, and particularly a starch-vinyl acetate copolymer, a polyvinyl alcohol, a styrene-butadiene latex, or the like.

The amount of the binder to be used can be selected 20 from a wide range, but it is generally preferable that the amount of the binder is about 5 to 30 wt.%, particularly about 10 to 20 wt.%, based on the undercoat layer.

The coating amount of the undercoat layer coating composition is 3 to 20 g/m², preferably about 5 to 12 g/m², 25 on dry weight basis, while the coating amount of the

protective layer coating composition is 0.5 to 10 g/m², preferably about 1 to 5 g/m², on dry weight basis.

The protective layer coating composition and undercoat layer coating composition are applied with a known coating device such as a bar coater, an air knife coater, a blade coater, a gravure coater, a die coater or the like. After the coating is dried, each layer can be treated with a super calender, a gloss calender or the like to impart smoothness to the surface.

It is also possible to provide a protective layer, an adhesive layer, a magnetic recording layer or the like on the rear side of the support. Also, various technologies known in the field of manufacturing heat-sensitive recording materials can be added, if so desired.

15

EXAMPLES

The present invention will be described in further detail with reference to examples, but the present invention is not limited to these examples. Unless otherwise specified, all "parts" and "%" indicate "weight parts" and "wt%," respectively. The average particle diameters are measured using an electron microscope.

Example 1

Preparation of undercoat layer coating composition

A composition composed of 60 parts of calcined clay (trade name: Ansilex, oil absorption 110 ml/100 g, made by Engelhard Corporation), 100 parts of a 20% dispersion of organic expandable hollow particles (inside diameter/outside diameter = 0.95; shell material = polyvinylidene chloride) which expand to an average particle diameter of about 5 μm upon expansion, 1 part of a 40% aqueous solution of a polyacrylic acid sodium salt, 14 parts of a styrene-butadiene latex with a solids concentration of 48%, 50 parts of a 10% aqueous solution of polyvinyl alcohol (degree of saponification: 88%, degree of polymerization: 1000) and 40 parts of water was mixed and stirred to obtain an undercoat layer coating composition.

Preparation of Dispersion A

A composition composed of 10 parts of N-p-toluene-sulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea, 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain Dispersion A.

Preparation of Dispersion B

A composition composed of 10 parts of a fluoran-based leuco dye which forms black color, i.e., 3-(N-ethyl-

p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C), 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain 5 Dispersion B.

Preparation of Dispersion C

A composition composed of 10 parts of 1,2-di(3-methylphenoxy)ethane, 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a 10 sand mill to an average particle diameter of 1.0 μm to obtain Dispersion C.

Preparation of Dispersion D

A composition composed of 40 parts of aluminum hydroxide (trade name: Higilite H42, made by Showa Denko, 15 average particle diameter of primary particles: 1 μm), 1 part of a 40% aqueous solution of a polyacrylic acid sodium salt and 40 parts of water was mixed and stirred to obtain Dispersion D.

Preparation of heat-sensitive recording layer coating

20 composition

120 parts of Dispersion A, 40 parts of Dispersion B, 80 parts of Dispersion C, 40 parts of Dispersion D, 160 parts of a 10% aqueous solution of polyvinyl alcohol (degree of polymerization: 100, degree of saponification: 25 98%), 20 parts of a styrene-butadiene latex with a solids

concentration of 50% and 12.5 parts of a 40% aqueous solution of glyoxal were mixed and stirred to obtain a heat-sensitive recording layer coating composition.

Preparation of protective layer coating composition

5 500 parts of a 10% aqueous solution of acetoacetyl-modified polyvinyl alcohol (trade name: Gohsefimer Z200, made by The Nippon Synthetic Chemical Industry Co., Ltd.), 40 parts of a 50% aqueous dispersion of kaolin (trade name UW-90, made by Engelhard Corporation) and 40 parts of a
10 50% aqueous dispersion of aluminum hydroxide (trade name: Higilite H42, made by Showa Denko) were mixed and stirred to obtain a protective layer coating composition.

Production of heat-sensitive recording material

One side of wood free paper (neutral paper) weighing
15 64 g/m² was coated with the above undercoat layer coating composition such that the coating amount was 7 g/m² on dry weight basis, and the coating was dried. This coated side was then brought into close contact with a chromium-plated, mirror-finish metal hot roll (120°C). This heat-treatment
20 caused the organic expandable particles to expand, whereby an undercoat layer was formed.

The undercoat layer thus formed was coated with the heat-sensitive recording layer coating composition such that the coating amount after drying was 6 g/m², and the
25 coating was dried to form a heat-sensitive recording layer.

The resulting heat-sensitive recording layer was then coated with the protective layer coating composition such that the coating amount after drying was 3 g/m² to obtain a heat-sensitive recording material. The heat-sensitive 5 recording material thus obtained was subjected to a surface smoothing treatment with a super calender.

Example 2

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that amorphous 10 silica (trade name Mizukasil P-603, made by MIZUSAWA INDUSTRIAL CHEMICALS, LTD.) was used in place of aluminum hydroxide in the preparation of Dispersion D in Example 1.

Example 3

A heat-sensitive recording material was obtained in 15 the same manner as in Example 1 except that kaolin (trade name UW-90, made by Engelhard Corporation, average particle diameter of primary particles: 1 μm) was used in place of aluminum hydroxide in the preparation of Dispersion D in Example 1.

20 Example 4

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that talc (trade name Hymicron, made by Takehara Kagaku Kabushiki Kaisha, average particle diameter of primary particles: 5 μm) was 25 used in place of aluminum hydroxide in the preparation of

Dispersion D in Example 1.

Example 5

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that 10 parts of 5 1,2-diphenoxymethane was used instead of 10 parts of 1,2-di(3-methylphenoxy)ethane in the preparation of Dispersion C in Example 1.

Example 6

A heat-sensitive recording material was obtained in 10 the same manner as in Example 1 except that 10 parts of 3-di(n-butyl)amino-6-methyl-7-anilinofluoran (melting point: 182°C) was used instead of 10 parts of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran in the preparation of Dispersion B in Example 1.

15 Example 7 Comparative Example 1

Preparation of undercoat layer coating composition

A composition composed of 40 parts of calcined clay (trade name: Ansilex, oil absorption 110 ml/100 g, made by Engelhard Corporation), 100 parts of a 40% dispersion of 20 organic hollow particles having an average particle diameter of 1.0 µm (inside diameter/outside diameter: 0.7, shell material: polystyrene), 1 part of a 40% aqueous solution of sodium salt of polyacrylic acid, 14 parts of a styrene-butadiene latex with a solids concentration of 48%, 25 50 parts of a 10% aqueous solution of polyvinyl alcohol

(degree of saponification: 88%, degree of polymerization: 1000), and 40 parts water was mixed and stirred to obtain an undercoat layer coating composition.

Preparation of Dispersion A

5 A composition composed of 10 parts of N-p-toluene-sulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea, 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain Dispersion A.

10 Preparation of Dispersion B

A composition composed of 10 parts of a fluoran-based leuco dye which forms black color, i.e., 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C), 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain Dispersion B.

Preparation of Dispersion C

20 A composition composed of 10 parts of 1,2-di(3-methylphenoxy)ethane, 5 parts of a 5% aqueous solution of methyl cellulose and 25 parts of water was pulverized in a sand mill to an average particle diameter of 1.0 μm to obtain Dispersion C.

Preparation of heat-sensitive recording layer coating composition

120 parts of Dispersion A, 40 parts of Dispersion B,
80 parts of Dispersion C, 160 parts of a 10% aqueous
solution of polyvinyl alcohol (degree of polymerization:
100, degree of saponification: 98%), 20 parts of a
5 styrene-butadiene latex with a solids concentration of 50%,
17 parts of precipitated calcium carbonate and 12.5 parts
of a 40% aqueous solution of glyoxal were mixed and
stirred to obtain a heat-sensitive recording layer coating
composition.

10 Preparation of protective layer coating composition

500 parts of a 10% aqueous solution of acetoacetyl-
modified polyvinyl alcohol (trade name: Gohsefimer Z200,
made by The Nippon Synthetic Chemical Industry Co., Ltd.),
40 parts of a 50% aqueous dispersion of kaolin (trade name
15 UW-90, made by Engelhard Corporation) and 40 parts of a
50% aqueous dispersion of aluminum hydroxide (trade name:
Higilite H42, made by Showa Denko) were mixed and stirred
to obtain a protective layer coating composition.

Production of heat-sensitive recording material

20 One side of wood free paper (neutral paper) weighing
64 g/m² was coated with the above undercoat layer coating
composition such that the coating amount was 9 g/m² on dry
weight basis, and the coating was dried, whereby an
undercoat layer was formed.

25 The undercoat layer thus formed was coated with the

heat-sensitive recording layer coating composition such that the coating amount after drying was 6 g/m², and the coating was dried to form a heat-sensitive recording layer.

The resulting heat-sensitive recording layer was then
5 coated with the protective layer coating composition such that the coating amount after drying was 3 g/m² to obtain a heat-sensitive recording material. The heat-sensitive recording material thus obtained was subjected to a surface smoothing treatment with a super calender.

10 Example 8 Comparative Example 2

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that a fluorane-based fluoran-based leuco dye capable of forming black color, namely 3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran (melting point: 227°C) was used instead of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation of Dispersion B in Example 7 Comparative Example 1.

20 Example 9 Comparative Example 3

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that a fluorane-based fluoran-based leuco dye capable of forming black color, namely 3-pyrrolidino-6-methyl-7-anilinofluoran (melting point: 225°C) was used

instead of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation of Dispersion B in Example 7 Comparative Example 1.

Example 10 Comparative Example 4

5 A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that a fluoran-based leuco dye capable of forming black color, namely 3-diethylamino-6-methyl-7-anilinofluoran (melting point: 192°C) was used instead of 10 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation of Dispersion B in Example 7 Comparative Example 1.

Example 11 Comparative Example 5

A heat-sensitive recording material was obtained in 15 the same manner as in Example 7 Comparative Example 1 except that a fluoran-based leuco dye capable of forming red color, namely 3-diethylamino-7,8-benzofluoran (melting point: 217°C), was used instead of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation of Dispersion B in Example 7 Comparative Example 1.

Example 12 Comparative Example 6

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 25 except that 10 parts of 2-naphthyl benzyl ether was used

instead of 10 parts of 1,2-di(3-methylphenoxy)ethane in the preparation of Dispersion C in Example 7 Comparative Example 1.

Example 13 Comparative Example 7

5 A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that 10 parts of di(p-methylbenzyl) oxalate was used instead of 10 parts of 1,2-di(3-methylphenoxy)ethane in the preparation of Dispersion C in Example 7

10 Comparative Example 1.

Example 14 Comparative Example 8

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that 10 parts of 2-(2'-hydroxy-5'-
15 methylphenyl)benzotriazole was used instead of 10 parts of 1,2-di(3-methylphenoxy)ethane in the preparation of Dispersion C in Example 7 Comparative Example 1.

Example 15 Comparative Example 9

20 A heat-sensitive recording material was obtained in the same manner as in Example 1 except that magnesium carbonate (trade name: Precipitated Magnesium Carbonate, made by Kyowa Chemical Industry Co., Ltd.) was used instead of aluminum hydroxide in the preparation of Dispersion D in Example 1.

Example 16 Comparative Example 10

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that Dispersion D was not used in the preparation of the heat-sensitive 5 recording layer coating composition in Example 1.

Comparative Example 1 Comparative Example 11

A heat-sensitive recording material was obtained in the same manner as in Example 1 except that 10 parts of 4-hydroxy-4'-isopropoxydiphenylsulfone was used instead of 10 parts of N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea in the preparation of Dispersion A in Example 1.

Comparative Example 2 Comparative Example 12

A heat-sensitive recording material was obtained in 15 the same manner as in Example 7 Comparative Example 1 except that 10 parts of bis(3-allyl-4-hydroxyphenyl)sulfone was used instead of 10 parts of N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)-phenylurea in the preparation of Dispersion A in Example 7

20 Comparative Example 1.

Comparative Example 3 Comparative Example 13

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that 10 parts of 2,4'-dihydroxydiphenylsulfone was 25 used instead of 10 parts of N-p-toluenesulfonyl-N'-3-

(p-toluenesulfonyl-oxy)phenylurea in the preparation of Dispersion A in Example 7 Comparative Example 1.

Comparative Example 4 Comparative Example 14

A heat-sensitive recording material was obtained in 5 the same manner as in Example 7 Comparative Example 1 that 10 parts of a fluoran-based dye capable of forming black color, i.e., 3-di(n-butyl)amino-6-methyl-7-anilinofluoran (melting point: 182°C) was used instead of 10 parts of 10 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation of Dispersion B in Example 7 Comparative Example 1.

Comparative Example 5 Comparative Example 15

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 15 except that 10 parts of a fluoran-based leuco dye capable of forming black color, i.e., 3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluoran (melting point: 164°C) was used instead of 10 parts of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C) in the preparation 20 of Dispersion B in Example 7 Comparative Example 1.

Comparative Example 6 Comparative Example 16

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that 10 parts of a phthalide compound capable of 25 forming blue color, namely 3-(4-diethylamino-2-

methylphenyl)-3-(4-dimethyl-aminophenyl)-6-dimethylaminophthalide (melting point: 217°C), was used as a leuco dye instead of 10 parts of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 5 206°C) in the preparation of Dispersion B in Example 7 Comparative Example 1.

Comparative Example 7 Comparative Example 17

A heat-sensitive recording material was obtained in the same manner as in Example 7 Comparative Example 1 except that a fluoran-based leuco dye capable of forming red color, namely 3-diethylamino-6-methyl-7-chlorofluoran (melting point: 235°C) was used instead of 3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 10 206°C) in the preparation of Dispersion B in Example 7 15 Comparative Example 1.

The heat-sensitive recording materials obtained above were subjected to the following evaluation tests, and the results are shown in Table 1.

20 Recording density

Using a thermosensitive printing tester (product name: TH-PMD, manufactured by Okura Denki Kabushiki Kaisha), each heat-sensitive recording material was colored at an applied energy of 0.50 mJ/dot, and the color 25 density of the recorded image thus obtained was measured

in visual mode with a Macbeth densitometer (trade name: model RD-914, made by Macbeth).

Heat resistance

After recording in the measurement of recording density, the heat-sensitive recording material was left to stand for 5 hours in a dryer maintained at 90°C, and then the optical density of the unrecorded portion was measured with a Macbeth densitometer to evaluate the heat resistance.

10 Light resistance

After recording in the measurement of recording density, the heat-sensitive recording material was left to stand for 24 hours in a xenon weatherometer (68 W/m² - 300 to 400 nm) maintained at 63°C and 40% RH, and then the optical density of the unrecorded portion and the optical density of the recorded image were measured with a Macbeth densitometer to evaluate the light resistance.

Water resistance

After recording in the evaluation of recording density, the heat-sensitive recording material was immersed for 24 hours in water at 20°C, and then the heat-sensitive recording material was allowed to dry naturally. The optical density of the recorded image was measured with a Macbeth densitometer to evaluate the water resistance.

Hot water resistance

After recording in the evaluation of recording density, the heat-sensitive recording material was immersed for 30 seconds in hot water at 90°C, and then the 5 heat-sensitive recording material was allowed to dry naturally. The optical density each of the unrecorded portion and the recorded image was measured with a Macbeth densitometer to evaluate the hot water resistance.

Plasticizer resistance

10 A wrap film (trade name: Hiwrap KMA-W, made by Mitsui Chemical) was wound 3-fold around a polypropylene pipe (40 mm diameter). A heat-sensitive recording material having formed images thereon was superposed on the film with the images directed outward and thereon was 15 further wound a wrap film three-fold. After standing at 40°C for 24 hours, the optical density of the images was measured with the above Macbeth densitometer, whereby the recording material was assessed for plasticizer resistance.

Table 1

	Heat-sensitive recording layer			Under-coat layer		Recording density		Heat-resist-ance	Light resistance	Water resist-ance	Hot water resistance	Plasticizer resistance
	Leuco dye (melting point °C)	Deve-loper pigment	Sensi-tizer	Pigment recorded portion	Un-recorded portion	Recorded portion	Un-recorded portion	Recorded portion	Un-recorded portion	Recorded portion	Un-recorded portion	Recorded portion
Ex. 1	LDK(206)	PF201 Al(OH) ₃	SA	EP	0.06	1.37	0.07	0.12	1.34	1.32	0.09	1.28
Ex. 2	LDK(206)	PF201 Silica	SA	EP	0.06	1.30	0.07	0.12	1.27	1.27	0.10	1.26
Ex. 3	LDK(206)	PF201 Kaolin	SA	EP	0.06	1.29	0.07	0.12	1.25	1.24	0.09	1.22
Ex. 4	LDK(206)	PF201 Talc	SA	EP	0.06	1.30	0.07	0.12	1.28	1.26	0.10	1.24
Ex. 5	LDK(206)	PF201 Al(OH) ₃	SB	EP	0.06	1.40	0.08	0.12	1.36	1.36	0.14	1.34
Ex. 6	ODI ₁ (182)	PF201 Al(OH) ₃	SA	EP	0.06	1.41	0.11	0.12	1.36	1.36	0.13	1.31
[[Ex. 7]] Comp. Ex. 1	LDK(206)	PF201 CaCO ₃	SA	HP	0.06	1.35	0.07	0.12	1.32	1.01	0.34	0.92
[[Ex. 8]] Comp. Ex. 2	LDKM(227)	PF201 CaCO ₃	SA	HP	0.06	1.30	0.07	0.12	1.27	1.00	0.32	0.92
[[Ex. 9]] Comp. Ex. 3	PS175 (225)	PF201 CaCO ₃	SA	HP	0.06	1.28	0.07	0.14	1.25	0.96	0.38	0.90
[[Ex. 10]] Comp. Ex. 4	ODI(192)	PF201 CaCO ₃	SA	HP	0.06	1.35	0.07	0.13	1.32	1.00	0.35	0.91
[[Ex. 11]] Comp. Ex. 5	PSP(217)	PF201 CaCO ₃	SA	HP	0.06	1.24	0.09	0.15	1.00	0.93	0.29	0.85
[[Ex. 12]] Comp. Ex. 6	LDK(206)	PF201 CaCO ₃	SC	HP	0.06	1.36	0.07	0.12	1.31	1.02	0.33	0.93
[[Ex. 13]] Comp. Ex. 7	LDK(206)	PF201 CaCO ₃	SD	HP	0.06	1.32	0.08	0.12	1.29	0.96	0.36	0.90

[[Ex.14]] Comp. Ex. 8	LDK (206)	PF201	CaCO ₃	SE	HP	0.06	1.30	0.07	0.11	1.29	1.01	0.35	0.91	1.26
[[Ex.15]] Comp. Ex. 9	LDK (206)	PF201	MgCO ₃	SA	EP	0.06	1.34	0.12	0.12	1.30	0.99	0.40	0.81	1.32
[[Ex.16]] Comp. Ex. 10	LDK (206)	PF201	None	SA	EP	0.06	1.36	0.13	0.12	1.32	1.30	0.26	1.29	1.31

Table 1 (continued)

Heat-sensitive recording layer			Under-coat layer		Recording density		Heat-resistance		Light resistance		Water-resistance		Hot water resistance		Plasticizer resistance
Leuco dye (melting point °C)	Deve- loper	Pigment	Sensi- tizer	Pigment	Un- recorded portion	Recorded portion	Plasticizer resistance								
Comp. Ex. [1]	LDK (206)	D-8	Al(OH) ₃	SA	EP	0.06	1.37	0.20	0.12	1.34	1.26	0.20	1.01	1.01	0.87
Comp. Ex. [2]	LDK(206)	TG-SH	CaCO ₃	SA	HP	0.07	1.36	0.26	0.16	1.25	1.01	0.38	0.91	0.91	1.28
Comp. Ex. [3]	LDK (206)	2,4'- BPS	CaCO ₃	SA	HP	0.06	1.26	0.15	0.14	1.20	0.92	0.31	0.86	0.86	1.21
Comp. Ex. [4]	ODII (182)	PF201	CaCO ₃	SA	HP	0.06	1.38	0.18	0.14	1.35	0.98	0.34	0.90	0.90	1.31
Comp. Ex. [5]	S-205 (164)	PF201	CaCO ₃	SA	HP	0.06	1.36	0.21	0.14	1.33	0.99	0.36	0.90	0.90	1.32
Comp. Ex. [6]	Phthalide (217)	PF201	CaCO ₃	SA	HP	0.06	1.29	0.26	0.15	1.23	0.93	0.35	0.84	0.84	1.21
Comp. Ex. [7]	PSD-VI (235)	PF201	CaCO ₃	SA	HP	0.06	1.18	0.10	0.18	1.12	0.81	0.29	0.78	0.78	1.11

The abbreviations in Table 1 stand for the meanings listed in Table 2 below.

Table 2

Abbreviation	Meaning
LDK	3-(N-ethyl-p-toluidino)-6-methyl-7-anilinofluoran (melting point: 206°C)
ODII	3-di(n-butyl)amino-6-methyl-7-anilinofluoran (melting point: 182°C)
LDKM	3-(N-ethyl-p-toluidino)-6-methyl-7-(p-toluidino)fluoran (melting point: 227°C)
PS175	3-pyrrolidino-6-methyl-7-anilinofluoran (melting point: 225°C)
ODI	3-diethylamino-6-methyl-7-anilinofluoran (melting point: 192°C)
PSP	3-diethylamino-7,8-benzofluoran (melting point: 217°C)
S-205	3-(N-ethyl-N-isoamylamino)-6-methyl-7-anilinofluoran (melting point: 164°C)
Phthalide	3-(4-diethylamino-2-methylphenyl)-3-(4-dimethylaminophenyl)-6-dimethylaminophthalide (melting point: 217°C)
PSD-VI	3-diethylamino-6-methyl-7-chlorofluoran (melting point: 235°C)
PF201	N-p-toluenesulfonyl-N'-3-(p-toluenesulfonyloxy)phenylurea
D-8	4-hydroxy-4'-isopropoxydiphenylsulfone
TG-SH	Bis(3-allyl-4-hydroxyphenyl)sulfone
2,4'-BPS	2,4'-dihydroxydiphenylsulfone
SA	1,2-di(3-methylphenoxy)ethane
SB	1,2-diphenoxymethane
SC	2-naphthyl benzyl ether
SD	di(p-methylbenzyl) oxalate
SE	2-(2'-hydroxy-5'-methylphenyl)benzotriazole
HP	hollow particles
EP	Expandable particles

As shown in Table 1, the heat-sensitive recording materials of the present invention exhibit excellent recording sensitivity, heat resistance of the unrecorded portion, and stability of the recorded image.